Studies on the Determination of Metals by the Extraction Method of Metal Organic Compounds. XI : Determination of Microamount of Iron in Aluminium, Magnesium, Zinc and Lead Metals

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Determination of Microamount of Iron in Aluminium, Magnesium, Zinc and Lead Metals*

Emiko SUDÔ

The Research Institute for Iron, Steel and Other Metals

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Synopsis

The microdetermination of iron by extraction of its complex with antipyrine and potassium thiocyanate by use of ethyl acetate, and photometry of the extract solution were applied to the determination of iron in aluminium, magnesium, zinc and lead metals, and this method was available for microdetermination, that is, 0.0002 per cent of iron in aluminium metal and up to 0.001 per cent of iron in magnesium, zinc and lead metals can be determined.

I. Introduction

It has previously been shown(1) that the complex of iron with antipyrine and ammonium thiocyanate is extracted with ethyl acetate and this extract solution shows the maximum absorption at 470 mμ. Application of this method to the photometric determination of microamount of iron in aluminium, magnesium, zinc and lead metals, by measuring the absorbance of the extract solution, was attempted and the results indicated that such determination is possible.

II. Experimental results

Apparatus: Beckman Model DU spectrophotometer, with 1 cm cell, was used.

Reagents were as follows:

Standard iron solution: A solution containing 10 γ/ml of Fe was prepared from electrolytic iron. Antipyrine solution: 5 per cent aqueous solution. Potassium thiocyanate solution: 20 per cent aqueous solution. Ethyl acetate: analytical grde. Hydrochloric acid: distilled.

Preparation of calibration curve: In a separatory funnel, 1~10 ml of the standard iron solution was placed, 3 ml of potassium thiocynate solution and 3 ml of antipyrine solution were added, and shaken with 5 ml of ethyl acetate. The ethyl acetate layer was separated, placed in 1 cm cell, and the absorbance was measured at 470 mμ. Relative curve of the amount of iron and absorbance was taken as the calibration curve, which is shown in Fig. 1.

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* The 849th report of the Research Institute for Iron, Steel and Other Metals.

(1) E. Sudô, J. Chem. Soc. Japan, **75** (1954), 968; Sci. Rep. RITU, **A7** (1955), 312.

1. Determination of iron in aluminium metal

(i) Procedure

A solution of 0.5~20 g of aluminium metal, dissolved in 20~40 ml of 6 N hydrochloric acid by heating, was placed in a volumetric flask of 50~500 ml, diluted to the mark with water, and 5~10 ml aliquot (content of Fe, less than 10 γ) of this solution was transferred to a separatory funnel. To this, each 3 ml of potassium thiocyanate solution and antipyrine solution were added, the mixture was shaken with 5 ml of ethyl acetate, and the acetate extract was transferred to the 1 cm cell. The absorbance at 470 mμ was measured and the amount of iron obtained from the calibration curve.

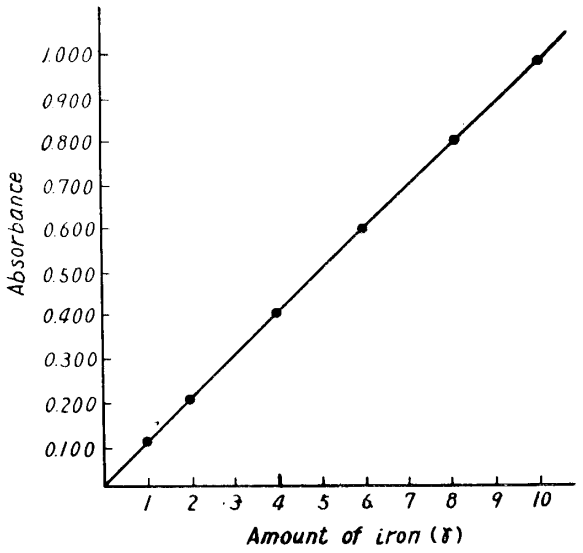

Fig. 1. Calibration curve for iron.

(ii) Analytical result

Table 1 gives the results obtained by the determination of iron by this method, using the mixed solution of spectroscopically pure aluminium and various amount of iron. These results have proved that the determination of iron is possible even if a small amount of iron is present, the determinable range being 0.0002~0.2 per cent.

Table 1. The analytical results for determination of microamount of iron in aluminum. (Synthetic sample)

Al taken (g)	Fraction	Iron added (γ)	Absorbance	Iron found (γ)	Iron (%)
1.9604	1/5	1.0	0.106	1.05	0.0002
1.0010	1/5	1.0	0.102	1.00	0.0005
0.5010	1/5	1.0	0.105	1.05	0.0010
0.5006	1/5	1.0	0.098	1.00	0.0009
0.5005	1/5	2.0	0.202	2.05	0.0040
1.0008	1/20	8.0	0.800	8.05	0.0160
0.2000	1/20	10.0	1.00	10.00	0.2000

The present method and the sulfosalicylic acid method were compared, using practical samples, and the results are presented in Table 2.

2. Determination of iron in magnesium metal

(i) Precedure

The analytical procedures were the same as in the case of aluminium metal.

(ii) Analytical results

Table 3 shows the results of the determination of iron by this method from metallic magnesium (99.9 per cent purity) to which a definite amount of iron was added. These results indicate that the amount of iron added was fully detected

and that the iron content of 0.001~0.2 per cent can be determined by the direct extraction from the acid solution, without separating magnesium.

The results of the determinations of iron in metallic magnesium by the present method and by the sulfosalicylic acid method are compared in Table 4.

Table 2. The comparison of the present method and the sulfosalicylic acid method for determination of iron in the aluminium sample.

Sample		Sample taken (g)	Fraction	Absorbance	Iron found (γ)	Iron (%)
A	Present method	0.5021 0.5080	1/20 1/20	0.872 0.884	8.82 8.95	0.035_1 0.035_2
	Sulfosalicylic acid method	0.9979 1.0016	— —	0.141 0.141	360 360	0.031 0.031
B	Present method	0.5061 0.5013	1/100 1/100	0.690 0.660	6.95 6.65	0.137_3 0.132_6
	Sulfosalicylic acid method	0.5038 0.5046	— —	0.280 0.285	650 650	0.130 0.131

Table 3. The analytical results for determination of microamount of iron in magnesium metal. (Synthetic sample)

Mg taken (g)	Fraction	Iron added (γ)	Absorbance	Iron found (γ)	Iron %
0.5163	1/20	1.0	0.102	1.0	0.0038
0.5165	1/20	2.0	0.200	2.0	0.0077
0.5170	1/20	5.0	0.502	5.0	0.0191
0.5160	1/20	8.0	0.801	8.0	0.0305
1.0012	1/10	1.0	0.103	1.0	0.0010
1.0019	1/10	2.0	0.201	2.0	0.0019
0.5002	1/100	8.0	0.800	8.0	0.1600
0.5005	1/100	10.0	1.100	10.0	0.2000

Table 4. The comparison of the present method and the sulfosalicylic acid method for determination of iron in metallic magnesium.

Method	Sample taken (g)	Fraction	Absorbance	Iron found (γ)	Iron (%)
Present method	1.0433 1.0436	1/40 1/40	0.350 0.363	3.5 3.6	0.013_4 0.013_8
Sulfosalicylic acid method	2.6397 2.4588	— —	0.162 0.175	380 410	0.014_3 0.017_0

3. Determination of iron in zinc metal

In the case of the metal containing above 0.02 per cent of iron, the preliminary removal of zinc is not necessery and the determination can be made by the direct extraction as in the case of aluminium metal. When the content of iron is less than 0.02 per cent, the most of zinc must be separated from iron. Iron in this

case is removed by filtration as its hydroxide, dissolved in acid, and this acid solution is submitted to the usual procedure.

(i) Procedure

About 8~10 g of the metal was dissolved in 120~180 ml of dilute aqua regia (nitric acid (1 : 1) 1 + hydrochloric acid 3 + distilled water 8) by heating, cooled, and heated after the addition of excess of ammonium hydroxide, it was warmed to coagulate the precipitate of iron hydroxide. After cooling, the precipitate was collected on a filter, and then dissolved in 10 ml of 6 N hydrochloric acid, and poured into a measuring flask of 100~250 ml, from which 5~10 ml of this solution was taken into a separatory funnel, and iron was determined according to the usual foregoing method.

(ii) Analytical results

Determination of iron was carried out by this procedure using pure zinc to which a definite amount of iron was added. As the results given in Table 5 show, a minute amount of iron can be determined by this procedure.

Table 5. The analytical results for determination of microamount of iron in zinc metal. (Synthetic sample)

Zn taken (g)	Iron added (mg)	Fraction	Absorbance	Iron found (mg)	Iron (%)
8.9260	0.100	1/20	0.510	0.102	0.0013
9.0070	0.100	1/20	0.520	0.104	0.0012
9.0123	0.200	1/50	0.424	0.210	0.0027
8.8246	0.200	1/50	0.450	0.225	0.0025

4. Determination of iron in lead metal

When the iron content is over 0.005 per cent, the determination can be made without the preliminary removal of lead; but when the content of iron is below 0.005 per cent, lead must be removed by filtration as lead sulfate and the filtrate submitted to the foregoing procedure. By this way, up to 0.001 per cent of iron can be determined in lead metal.

(i) Procedure

A solution of 1.0~0.5 g of the metal was dissolved in 10 ml of nitric acid (1 + 4) by heating (when the content of iron is below 0.005 per cent, sulfuric acid is added to this solution and it was heated until white fumes begin to evolve and iron can be separated from lead by filtration as lead sulfate) and the solution was transferred to a 50~250 ml volumetric flask, made up to the mark with water, 10 ml of this solution is taken into a separatory funnel and the procedures thereafter are the same as in the foregoing cases.

(ii) Analytical results

Table 6 gives the results obtained from the determination of iron by the present procedure using pure lead to which a definite amount of iron was added. The amount of iron added is fully detected and the results confirm that the determination of a minute amount of iron in lead is possible.

Table 6. The analytical results for determination of microamount of iron in lead metal. (Synthetic sample)

Pb taken (g)	Iron added (γ)	Fraction	Absobance	Iron found (γ)	Iron (%)
1.0210	10.0	1/5	0.102	10.0	0.0010
0.5002	10.0	1/5	0.101	10.0	0.0019
0.5012	15.0	1/5	0.301	15.0	0.0030
0.5005	25.0	1/5	0.502	25.0	0.0049

5. Interfering elements

The chief elements which interfere in the determination of iron in aluminium, magnesium, zinc and lead metals are copper and bismuth. The permissible range of copper is up to 80 per cent of the iron amount and that of bismuth is about the same amount as iron. Above these amounts, copper and bismuth must be removed with hydrogen sulfide.

Summary

(1) A minute amount of iron in aluminium, magnesium, zinc and lead metals was determined by converting iron to a complex with antipyrine and ammonium thiocyanate, extracting this complex with ethyl acetate, and submitting this extract to photometric determination.

(2) By the present method, 0.0002~0.2 per cent of iron in aluminium metal and 0.001~0.2 per cent of iron in magnesium, zinc and lead metals can be determined.

(3) Chief elements which interfere in this determination are copper and bismuth. The presence of copper up to 80 per cent of iron amount and of bismuth up to the same amount as iron may be permitted.

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